Weak hyperfine structure measurement using the magnetic repolarization effect: Application to N = 1 v = 1 (1s 3d)1Σ level of H2

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Weak hyperfine structure measurement using the magnetic repolarization effect: Application to $N = 1$ $v = 1$ $(1s\,3d)^1\Sigma$ level of H_2

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The magnetic repolarization effect is studied in the case where the hyperfine structure $(A\mathbf{I}\cdot\mathbf{J})$ of the considered excited atomic or molecular level is weaker than the natural width Γ. General expressions are given. It is shown that the amplitude of this effect varies as $(A/\Gamma)^2$ and that its value permits the determination of A when one compares the magnetic repolarization and depolarization effects. Such an effect is experimentally studied in the $N=1$, $v=1$ $(1s\,3d)^1\Sigma$ level of H_2. A value of $A=1\pm0.17)$ MHz is deduced, corresponding to $A/\Gamma=0.15$.

I. INTRODUCTION

Several kinds of experiments have been used to measure fine (fs) or hyperfine (hfs) structures of excited atomic or molecular states. The choice of the technique depends mainly upon the order of magnitude of the structure. When the structure is larger than the Doppler width one can use the oldest of these methods, namely optical spectroscopy. When the fs or hfs is smaller than the Doppler width but larger than the natural width, several related experiments have been widely used, the most common being optical detection of magnetic resonance[1] and nonzero field level crossing.[2]

Other related experiments are, for example, quantum beats,[3-7] which are useful mainly in beam foil spectroscopy, and, in cases such as hydrogen-like[8-9] or polar molecules,[10] where there is a quasidegeneracy of opposite parity levels, electric dipole resonance and electric field anticrossing.[9-10] After Fourier transformation of the experimental curves in the case of quantum beats, these experiments give resonance-like curves the width of which (limiting width in cases of resonance or electric field anticrossing experiments) is given by the natural lifetime of the level, and whose position is given by the structure. These methods have been applied to atoms and recently extended to homopolar molecules[11-13] and dipolar molecules.[10]

Another kind of experiment, the magnetic repolarization effect, gives a curve the width of which is determined by the structure itself. This effect, known for a very long time[14] has been recently used[15] in alkali atoms to measure hfs much larger than the natural width, by fitting theoretical and experimental curves. Because this effect does not give the sharp natural width-limited resonance like signal as in the other cases, but a broad signal whose width is given by the structure, it has been of very limited use in the past.

We wish to discuss in this paper (Sec. II) methods using a magnetic field intended to measure structures A smaller than the natural width Γ. This study was undertaken because we had detected experimentally a magnetic repolarization effect corresponding to a very weak hyperfine structure in the $N=1$, $v=1$ $(3d)^1\Sigma$ level of H_2 which is discussed in Sec. III.

In the case of structure smaller than natural width, the measured width in all the above mentioned experiments (crossing and anticrossing a like) is given roughly by the natural width and is relatively insensitive to the structure (some limiting cases of crossing experiments have been made for Cd,[16] Na, and K,[17] where $A\sim\Gamma$ and where all crossings overlap).

Two previous experiments have been used to measure a hfs smaller than Γ, but they both need optical pumping of the fundamental level, and are therefore not possible to carry out in the molecular case where no unambiguous optical pumping experiment has been reported.

The first was described by Lehmann[18] who optically pumped cadmium vapor on the singlet $^1S\rightarrow{}^1P$ resonance line. Owing to hyperfine coupling in the excited state, there is a shift of the ground state resonance. The sign of this shift is reversed on changing from σ_+ to σ_- excitation and its magnitude is proportional to A/Γ when $A<\Gamma$. He also observed modulated components related to the structure in the ground state resonance signal. But this method is limited to optically pumped resonance lines.

A somewhat less restrictive method has been described by Stoeckel.[19] The ground state of a vapor of ^{3}He is optically pumped. A discharge in the cell populates and aligns all the excited levels. It was shown that there is a signal resulting from the combination of the ground state nuclear orientation and the excited state electronic alignment, the width of which gives no information (being determined essentially by Γ when $A<\Gamma$) but the amplitude of which is proportional to A/Γ.

In the Sec. II of this paper we study the various signals which appear upon application of a static magnetic field to an aligned or oriented level with a small hyperfine structure. We show that their widths give no information, but their amplitudes enable us to measure A/Γ. We classify them according to the power in A/Γ to which these amplitudes are proportional. We show that the simplest repolarization signal is of order $(A/\Gamma)^2$. The corresponding experiments, in contrast to the two above mentioned experiments, does not need optical pumping and is therefore applicable to the molecular case.

In Sec. III, we describe some preliminary experi-

ments we have performed to measure very weak hfs in several vibrational and rotational levels of the $(3d)^1\Sigma$ level of H_2, using the above-mentioned repolarization effect.

II. THEORY

A. General

In this part we establish the general expression for the density matrix component when a magnetic field **H** is applied and when the hfs is weak. We discuss variation of these components with **H** according to the order in A/Γ.

1. *Density matrix as a function of* **H**

The considered excited level is characterized by **J**, the total electronic momentum (which is equal to **N**, the total rotational momentum in the singlet molecular case), **I** the nuclear spin. We study the general case which takes into account the molecule–molecule collision processes and therefore Γ is no longer only a scalar equal to τ^{-1} (where τ is the lifetime of the excited state) but a pressure dependent matrix which tends to the scalar τ^{-1} when the pressure tends to zero. Here we develop fully only the case in which the hfs Hamiltonian is $A\,\mathbf{I}\cdot\mathbf{J}$ (no quadrupolar interaction is considered) because it corresponds to our experimental situation (see Appendix). The more general case, could be treated by the same method. The static magnetic field **H** is chosen as quantization axis (oz). Calculations are carried out in the decoupled basis $|IJm_Im_J\rangle$ which is the proper basis when no hfs exists. For convenience we develop the density matrix ρ in its tensorial components, using the tensorial conventions given by Omont[20]:

$$ {}^{IJ}\rho = \sum_{k\chi q\sigma} {}^{IJ}\rho_{q\sigma}^{k\chi}\, {}^{JJ}T_q^k\, {}^{II}T_\sigma^\chi \quad . \tag{1}$$

The polarization of the emitted light after deexcitation of the J level $(J \to J_0)$ is related to the components of the light intensity, $I(\mathbf{e})$, which in turn is related to these tensorial components through the D'yakonov[21] expression, transposed to Omont's notation. {The tensorial components f_q^k defined by D'yakonov[21] are related to the ρ_q^k defined by Omont[20] in the following way: $f_q^k = [(2J+1)/(2k+1)]^{1/2}\rho_{-q}^k$}.

$$ I(\mathbf{e}) = I_0 \sum_{kq} (-)^q B_k\, {}^{JJ}\rho_q^k \phi_q^k(\mathbf{e}) \quad , \tag{2}$$

where $\phi_q^k(\mathbf{e})$ is the geometrical function of $\mathbf{e}$, the unit vector along the polarization, defined by D'yakonov,[21] where

$$ B_k = (2J+1)^{1/2}(2k+1)^{1/2} \begin{Bmatrix} 1 & 1 & k \\ J & J & J_0 \end{Bmatrix} ,$$

and

$$ {}^{JJ}\rho_q^k = \sum_{\chi\sigma} {}^{IJ}\rho_{q\sigma}^{k\chi}\, \mathrm{Trace}_I({}^I T_\sigma^\chi) = \frac{1}{(2I+1)^{1/2}}\, {}^{IJ}\rho_{q\,\sigma=0}^{k\,\chi=0} \quad . \tag{3}$$

This last relation comes from the fact that the emission (or absorption) of light corresponds to an electric dipole transition, which is independent of the spin distribution.

The density matrix ρ is the stationary solution of the time dependent equation

$$ \frac{d\rho}{dt} = -i[\mathcal{H}, \rho] - \Gamma\rho + \rho_{ex} \quad , \tag{4}$$

where

$$ \mathcal{H} = g_J \mu_B \mathbf{H}\cdot\mathbf{J} + g_I \mu_B \mathbf{H}\cdot\mathbf{I} + A\,\mathbf{I}\cdot\mathbf{J}$$

and where $\Gamma\rho$ represents the destruction of the state due to spontaneous emission or isotropic collisions, and ρ_{ex} represents the excitation process. Because of the different order of magnitude of the nuclear and electronic g factor $(g_I \ll g_J)$ we neglect the nuclear Zeeman effect compared to the electronic term.

In order to solve Eq. (4), we develop ρ in tensorial components using (1), multiply the two members of (4) by ${}^{JJ}T_q^{k\dagger}\, {}^{II}T_\sigma^{\chi\dagger}$ and take the trace. We obtain

$$ \frac{d}{dt}\, {}^{IJ}\rho_{q\sigma}^{k\chi} = -iq\omega\, {}^{IJ}\rho_{q\sigma}^{k\chi} - iA \sum_{k'\chi'q'\sigma'} \mathfrak{L}_{qq'\sigma\sigma'}^{kk'\chi\chi'}\, {}^{IJ}\rho_{q'\sigma'}^{k'\chi'} - \Gamma^k\, {}^{IJ}\rho_{q\sigma}^{k\chi} + {}^{IJ}\rho_{ex\,q\sigma}^{k\chi} \quad , \tag{5}$$

where

$$ \omega = g_J \mu_B H_z \quad ,$$

$$ \mathfrak{L}_{qq'\sigma\sigma'}^{kk'\chi\chi'} = \mathrm{Trace}([\mathbf{I}\cdot\mathbf{J},\ {}^{JJ}T_{q'}^{k'}\, {}^{II}T_{\sigma'}^{\chi'}]\, {}^{JJ}T_q^{k\dagger}\, {}^{II}T_\sigma^{\chi\dagger})$$

$$ = \left(\frac{(2k+1)(2k'+1)(2\chi+1)(2\chi'+1)}{I(I+1)(2I+1)J(J+1)(2J+1)}\right)^{1/2} \times \begin{Bmatrix} k' & 1 & k \\ J & J & J \end{Bmatrix} \begin{Bmatrix} \chi' & 1 & \chi \\ I & I & I \end{Bmatrix} (-)^{2I+\sigma+2J+q} \times [1-(-)^{k+k'+\chi+\chi'}] \sum_{Q=-1}^{+1} (-)^Q \begin{pmatrix} k' & 1 & k \\ q' & Q & -q \end{pmatrix} \begin{pmatrix} \chi' & 1 & \chi \\ \sigma' & -Q & -\sigma \end{pmatrix},$$

and where Γ^k is the kth tensorial component of Γ, equal to the inverse of the destructuion time of the ρ^k component. The coefficients $\mathfrak{L}$ are nonzero when

(i) The $3j$ coefficients are nonzero, which implies that $\sigma - \sigma' = q' - q = Q = 0, \pm 1$: the quantity $(\sigma + q)$ is conserved.

(ii) The $6j$ coefficients are nonzero: $k - k' = 0 \pm 1$ and $\chi - \chi' = 0 \pm 1$

(iii) $(k + k' + \chi + \chi')$ is odd

(iv) The two last conditions [(ii) and (iii)] imply that if $k' = k$ we must have $\chi' = \chi \pm 1$ and vice versa.

Equation (5) is valid for any value of the hfs constant A but can be solved only by numerical methods in the general case. In the case of weak hfs $(A < \Gamma)$ we can express the stationary solution of (5) as a series in $\rho_{q\sigma}^{k\chi}$ in powers of A

$$ {}^{IJ}\rho_{q\sigma}^{k\chi} = {}^{(0)}\rho_{q\sigma}^{k\chi} + A\, {}^{(1)}\rho_{q\sigma}^{k\chi} + A^2\, {}^{(2)}\rho_{q\sigma}^{k\chi} + \cdots \quad . \tag{6}$$

Injecting this solution into (5) and collecting powers of A we obtain the following results:

$$ {}^{(0)}\rho_{q\sigma}^{k\chi} = \frac{1}{\Gamma^k + iq\omega}\, \rho_{ex\,q\sigma}^{k\chi} \quad ,$$

$$ {}^{(1)}\rho_{q\sigma}^{k\chi} = \frac{-i}{\Gamma^k + iq\omega} \sum_{k'\chi'q'\sigma'} \mathfrak{L}_{qq'\sigma\sigma'}^{kk'\chi\chi'} \frac{1}{\Gamma^{k'} + iq'\omega}\, \rho_{ex\,q'\sigma'}^{k'\chi'} \quad ,$$

$$ {}^{(2)}\rho_{q\sigma}^{k\chi} = \frac{(-)}{\Gamma^k + iq\omega} \sum_{k'\chi'q'\sigma'} \mathfrak{L}_{qq'\sigma\sigma'}^{kk'\chi\chi'} \frac{1}{\Gamma^{k'} + iq'\omega}$$

$$\times \sum_{k''\chi''q''\sigma''} \mathcal{L}^{k'k''\chi'\chi''}_{q'q''\sigma'\sigma''} \frac{1}{\Gamma^{k''}+iq''\omega} \rho_{ex\,q''\sigma''}^{k''\chi''} \quad .$$

We are now able to discuss the dependence of a detected signal on the successive powers of A, when a magnetic field is applied, in different types of experiments.

2. Discussion

The discussion of each term of the development of $\rho(6)$ will now permit one to see under what conditions of excitation and detection (i.e., the determination of $\rho_{ex\,q\sigma}^{k\chi}$ and $\rho_{q\sigma}^{k\chi}$ respectively) it is possible to observe a signal as a function of the magnetic field H_z and of the hf structure. This will enable us by the way to classify some previously described experiments.

In all following experiments an optical transition starting from the J level is observed; the intensity of light components $I(\mathbf{e})$ is detected. This quantity is given by (2), (3), and (6). Thus the detected signal is related to the $\rho_{q\,\sigma=0}^{k\,\chi=0}$ components.

In order to clarify the discussion, we briefly recall some common definitions and some well known results:

The population of a $|IJ\rangle$ level is proportional to $\rho^{k=0\,\chi=0}$;

The electronic (or nuclear) orientation of the level is proportional to the $\rho_q^{k=1}$ components (or $\rho_\sigma^{\chi=1}$): the ρ_0^1 component, proportional to $\langle J_z\rangle$, represents an orientation parallel to oz, and $\rho_{\pm1}^1$, an orientation perpendicular to oz.

The electronic alignment is proportional to the $\rho_q^{k=2}$ components: ρ_0^2, proportional to $\langle 3J_z^2 - J^2\rangle$, represents an alignment parallel to oz; $\rho_{\pm2}^2$, an alignment perpendicular to oz.

An electronic or optical excitation process, which implies only electric interactions, does not perturb the initial nuclear spin distribution ρ_σ^χ.

During an excitation by an electron beam, the only nonzero tensorial components excited are[22]: $\rho_{ex\,0}^{k}$, when k is even if the beam is parallel to the oz quantization axis; $\rho_{ex\,q}^{k} = \rho_{ex\,-q}^{k}$ when both k and q are even, if the beam is perpendicular to oz.

a. Zero order. The well known Hanle effect[23] (magnetic depolarization effect) corresponds to a zero order effect. In the classical experiment, the J momentum is aligned perpendicular to H_z, the spin distribution being isotropic (the nonzero excitation components are $\rho_{ex\,00}^{00}$, $\rho_{ex\,00}^{20}$ and $\rho_{ex\,20}^{20} = \rho_{ex\,-20}^{20}$. The polarization P of the emitted light

$$P = \frac{I(\mathbf{oz}) - I(\mathbf{ox})}{I(\mathbf{oz}) + I(\mathbf{ox})} \quad , \tag{7}$$

depends on the magnetic field through the ${}^{(0)}\rho_{\pm20}^{20}$. The value $q = \pm2$ implies that the polarization as a function of H_z is Lorentzian, with full width at half height equal to

$$\Delta H = \Gamma^{k=2}/2g_J\mu_B \quad . \tag{8}$$

A variant of this effect can be obtained if we create and detect an electronic alignment at 45° with oz (creation and detection of the $\rho_{\pm10}^{20}$), or if we create and detect an electronic orientation at 90° with oz (creation and detection of the $\rho_{\pm10}^{10}$); in both cases the detected signal as a function of H_z is a Lorentzian of width $2\Delta H$, corresponding to the fact that $q = \pm1$.

b. First order. The first order variation of the density matrix, ${}^{(1)}\rho$, with H_z has been used by Stoeckel[19] in order to determine a weak hf structure ($A = 0.05\Gamma$) in the $(1s\,3p)^1P$ of ^{3}He. In the experiment, the ^1P level is excited in such a way that the nuclear spin is oriented parallel to oz ($\chi' = 1$, $\sigma' = 0$) and J is aligned perpendicularly ($k' = 2$, $q' = 0, \pm2$). The variation of the linear polarization of the emitted light, perpendicular to oz, when one destroys this nuclear orientation is then monitored so that the signal is proportional to the part of the $\rho_{\pm20}^{20}$ which is induced by the $\rho_{ex\,\pm20}^{21}$ component of the excitation. Under such excitation conditions the ${}^{(0)}\rho_{\pm20}^{20}$ component is zero (because $\Delta\chi = 1$), and the first order ${}^{(1)}\rho_{\pm20}^{20}$ is nonzero.

Similar types of experiments were envisaged by Stoeckel[24] with similar excitation ($\chi' = 1$, $\sigma' = \pm1$ and $k' = 2$, $q' = \pm1$). We note that if $\chi' = 0$ (no nuclear polarization in the excitation) and if $\chi = 0$ (optical detection), the selection rules show that there is no first order effect.

c. Second order. A second order effect in A/Γ has been described by Laloe[25] and detected on certain levels of ^{3}He, despite the large value of the hfs. This experiment consists of isotropically exciting the J momentum and orienting the nuclear spin parallel to oz ($\rho_{ex\,00}^{01} \neq 0$); the orientation parallel to oz of the emitted optical transition is then detected, corresponding to ρ_{00}^{10}. The ${}^{(0)}\rho_{00}^{10}$ and ${}^{(1)}\rho_{00}^{10}$ are equal to zero because $(k - k')$ and $(\chi - \chi')$ must simultaneously be equal to 1 [condition (iv)] and the observed signal is proportional to $A^2\,{}^{(2)}\rho_{00}^{10}$.

Another well known second order effect is the repolarization effect. Here the excitation is applied in such a way that the J momentum acquires an anisotropic distribution whose symmetry axis is oz, the nuclear spin I keeping its initial isotropic distribution (i.e., $\rho_{ex\,00}^{00} \neq 0$ and $\rho_{ex\,00}^{k0} \neq 0$, with $k \neq 0$); the signal is a function of the ρ_{00}^{k0} which depends on the magnetic field through a term in $(A/\Gamma)^2$.

The case where J is oriented ($k = 1$) can be achieved by optical excitation with circularly polarized light. This experiment has been carried out by R. Gupta *et al.*[15] in the case of strong hfs ($A \gg \Gamma$). The case where J is aligned (Fig. 1)(corresponding to $k = 2$) can be obtained by excitation with linearly polarized light, or with an electron beam parallel to oz. This experiment is reported here and we wish to establish in this last case the analytical expression of the detected signal for any value of I and J. In this experiment, the polarization P given by (7) of the emitted light is detected in a direction perpendicular to oz. Using the $I(\mathbf{e})$ expression (2), we can express P as a function of the ρ_{q0}^{k0}. In this expression, the $\rho_{\pm20}^{20}$ are equal to zero because of the condition (*i*) (which implies $\sigma + q = \sigma_{ex} + q_{ex}$), of the type of excitation ($\sigma_{ex} + q_{ex} = 0$) and of the type of optical detection ($\sigma = 0$), which together impose $q = 0$. We obtain

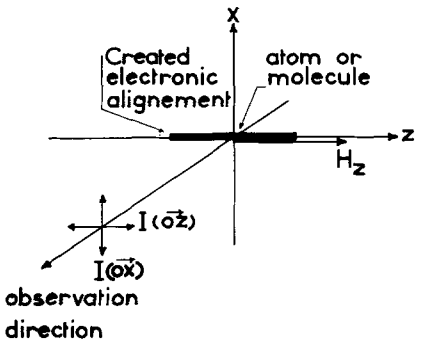

FIG. 1. Excitation and detection in the repolarization effect.

$$P = -\frac{1}{3} - \frac{4}{3\sqrt{10}} \frac{B_2}{B_0} \frac{\rho_{00}^{20}}{\rho_{00}^{00}} \quad . \tag{9}$$

Let us now see how these components vary with the magnetic field using the expansion of ρ to second order in A(6). In zero order, the ${}^{(0)}\rho_{00}^{00}$ and ${}^{(0)}\rho_{00}^{20}$ are nonzero, but independent of the magnetic field because $q = 0$. In first order, the selection rules require that the ${}^{(1)}\rho_{00}^{k0}$ components be equal to zero. In second order, ${}^{(2)}\rho_{00}^{00}$ and ${}^{(2)}\rho_{00}^{10}$ are equal to zero, and ${}^{(2)}\rho_{00}^{20}$ is function of H_z through ω:

$$ {}^{(2)}\rho_{00}^{20} = -\frac{1}{(\Gamma^{k=2})^2} \mathcal{L}_{010-1}^{2201} \mathcal{L}_{10-10}^{2210} \left(\frac{1}{\Gamma^{k=2} + i\omega} + \frac{1}{\Gamma^{k=2} - i\omega} \right) \rho_{ex}{}_{00}^{20} $$

$$ = \frac{\text{Const.}}{\Gamma^{k=2}} \left(\frac{1}{(\Gamma^{k=2})^2 + \omega^2} \right) \quad . \tag{10}$$

Using the preceding considerations, we obtain for the polarization P given by (9):

$$P(H_z, A) = \alpha \left[\beta + \left(\frac{A}{\Gamma^{k=2}} \right)^2 \frac{1}{(1+x^2)} \right] \text{ with } x = \omega/\Gamma^{k=2} \quad . \tag{11}$$

The detected polarization (Fig. 2) as a function of H_z is a Lorentzian curve whose amplitude varies as $(A/\Gamma^{k=2})^2$ and whose full width at half height is double the Hanle width given by (8). The α and β parameters can be expressed as a function of the excitation components ρ_{ex}, or as a function of the polarization P at high and zero fields:

$$P(H_z, A) = P(H_z = \infty, A) - \{[P(H_z = \infty, A) - P(H_z = 0, A)]\} \times \frac{1}{1+x^2} \quad .$$

By substituting explicit values of α and β we could obtain the amplitude of the repolarization effect as a function of I and J. However, the resulting expression would be valid only for weak A values and we prefer to establish in the next paragraph the quantities $P(H_z = \infty)$ and $P(H_z = 0)$ for any value of A, after discussing the physical interpretation of the repolarization effect.

d. Third order. The expression for the ${}^{(3)}\rho_{q0}^{kx}$ components is easily obtained from the ${}^{(2)}\rho_{q0}^{kx}$. Two previous experiments show an effect in the third order in A/Γ.

F. Laloe[25] describes an experiment where some nuclear orientation is created, J being isotropically excited ($\rho_{ex}{}_{00}^{01} \neq 0$) and where the electronic alignment, parallel to oz, is detected (ρ_{00}^{20}). The zero, first and second order of the development (6) of ρ are equal to zero, due to the selection rules. The detected signal varies with H_z in the third order in A/Γ. As pointed out above, this experiment was not performed in the case of weak hfs.

J. C. Lehman,[18] in an experiment performed in the 5^1P_1 level of Cd, excites this level in such a way that J is aligned parallel to H_z, I remaining isotropic ($\rho_{ex}{}_{00}^{20} \neq 0$) and he detects the electronic orientation parallel to H_z (ρ_{00}^{10}). The first nonzero term in the expansion (6) of this component is ${}^{(3)}\rho_{00}^{10}$ and therefore the detected signal is proportional to $(A/\Gamma)^3$.

B. Repolarization effect

The purpose of the present section is to establish the amplitude of this effect as a function of A and there to describe the experimental procedure used to determine A. In part 1 we present the physical interpretation of this effect based on a vectorial model, which is useful to show the basis of our calculation of the amplitude. In part 2, this calculation is carried out.

1. Vectorial model

The atom is anisotropically excited by polarized light or by an electron beam. This excitation, based on electrostatic interactions does not act on the spin which keeps an isotropic distribution, and the anisotropic character is transferred to J. After an average time of the order of the lifetime τ of the excited state, the emitted light corresponding to an electric dipole transition presents a polarization state P proportional to the J distribution at $t = \tau$. We wish to see how this distribution is influenced by the hyperfine interaction A and by a static magnetic field H_z, parallel to the direction of the initial anisotropy. For the sake of simplicity we take the case where J is oriented ($\langle J_z \rangle \neq 0$). In zero magnetic field two cases exist:

(i) The hf coupling is zero ($A = 0$); the J distribution does not change during the lifetime: $\langle J_z \rangle_{t=\tau} = \langle J_z \rangle_{t=0}$; the polarization ratio $P(A = 0)$ is then proportional to the initial J distribution: $\langle J_z \rangle_{t=0}$. The same result would be obtained if $I = 0$.

(j) hf coupling exists ($A \neq 0$); I and J precess around their resultant F. At the moment of emission the J orientation, $\langle J_z \rangle_{t=\tau}$, is given by projecting the initial

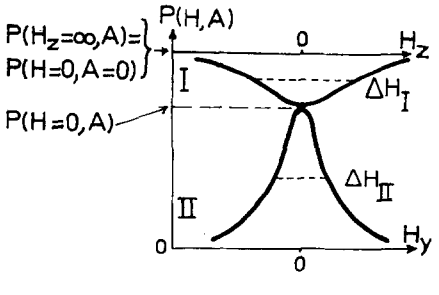

FIG. 2. Polarization ratio as a function of successively H_z (corresponding to P_I) in the repolarization effect, and $H_y(P_{II})$ in the Hanle effect, in the case of weak hfs ($A \ll \Gamma$). $\Delta H_I = 2\Delta H_{II} = \Gamma^{k=2}/g_J\mu_B$.

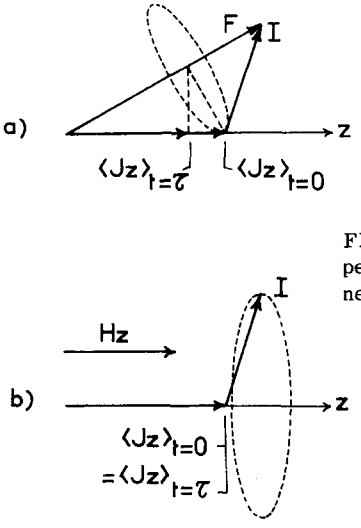

FIG. 3. Perturbation of hyperfine coupling by strong magnetic field ($g\mu_B H_z \gg A$).

orientation successively on **F** then on oz. This mean value is represented on Fig. 3(a) for an arbitrary I direction. This quantity is therefore smaller than the initial orientation $\langle J_z\rangle_{t=0}$. This corresponds to the fact that part of the J orientation has been transferred to the spin through the hf coupling. This result implies that the polarization ratio of the emitted light, proportional to $\langle J_z\rangle_{t=\tau}$, is weaker when a hfs exists.

If a magnetic field is applied along oz, the hf coupling is perturbed and the polarization ratio P in the two preceding cases is affected as follows:

(ii) $A=0$, the magnetic field does not act on $\mathbf{J}_z$ and the polarization ratio $P(H_z, A=0)$ is then independent of H_z and proportional to $\langle J_z\rangle_{t=0}$; we therefore have $P(H_z, A=0) = P(H_z=0, A=0)$.

(jj) $A\neq 0$, H_z tends to decouple **I** and **J**. At low magnetic field ($g\mu_B H_z \ll A$) the resulting momentum F slowly precesses around the small magnetic field, and the mean z component of **J** is therefore smaller than the initial value $\langle J_z\rangle_{t=0}$. When H_z increases **I** and **J** precess faster around H_z than around **F**, which is no longer a good quantum number, and P increases with H_z. At high field ($g\mu_B H_z \gg A$), here symbolized by $H_z=\infty$) the initial orientation, parallel to H_z is tightly bound to the oz axis (complete decoupling of I and J) and at all times, the mean z component of **J** is equal to the initial value [Fig. 3(b)].

In consequence, the polarization $P(H_z=\infty, A)$, related to $\langle J_z\rangle_{t=\tau}$ is equal to the polarization $P(H_z=0, A=0)$ related to $\langle J_z\rangle_{t=0}$. This equality (Fig. 2) will now be used to establish the amplitude of the repolarization effect given by:

$$P(H_z=\infty, A) - P(H_z=0, A) = P(H_z=0, A=0) - P(H_z=0, A) \tag{12}$$

2. *Amplitude of the repolarization effect*

The calculation of the repolarization effect amplitude given by (12) requires a knowledge only of the expression for $P(A)$ defined by (7) in zero magnetic field. The following calculation is valid for any order of magnitude of A; for this reason the $I(\mathbf{e})$ light components are now expressed as a function of the ${}^{FF}\rho_q^k$ components of the density matrix defined in the coupled basis, $\mathbf{F}=\mathbf{I}+\mathbf{N}$, which is the proper basis. In contrast to the preceding calculation where $H\neq 0$, it is now easy to solve the density matrix equation expressed in this basis in the case where $H=0$.

The light components $I(\mathbf{e})$ from the optical $J\rightarrow J_0$ transition are expressed in this coupled basis using the following D'yakonov expression[26] transposed to Omont's notation[20]

$$I(\mathbf{e}) = I_0 \sum_{FF'kq} (-)^q B_k {}^{FF'}\rho_q^k \phi_q^k(e) \ , \tag{13}$$

with

$$B_k = (-)^{2J+J_0+I+k+F'} [(2k+1)(2F+1)(2F'+1)]^{1/2} \times \begin{Bmatrix} 1 & 1 & k \\ J & J & J_0 \end{Bmatrix} \begin{Bmatrix} F & F' & k \\ J & J & I \end{Bmatrix}.$$

The summation on the F levels corresponds to the fact that the hfs is not optically resolved. The ${}^{FF'}\rho_q^k$ components are the stationary solution of equation (4) with $H_z=0$:

$${}^{FF'}\rho_q^k = \frac{1}{\Gamma^k + i(E_F - E_{F'})} {}^{FF'}\rho_{ex\,q}^{\ k} \ , \tag{14}$$

with

$$E_F - E_{F'} = \tfrac{1}{2}A[F(F+1) - F'(F'+1)]$$

The excitation density matrix ${}^{FF'}\rho_{ex}$ defined in the $I\times N$ space product, is related[27] to ${}^{JJ}\rho_{ex}$ defined in the J space by

$${}^{FF'}\rho_{ex\,q}^{\ k} = (-)^{F'+J+I+k} \frac{1}{2I+1} \left(\frac{(2F+1)(2F'+1)}{2k+1}\right)^{1/2} \times \begin{Bmatrix} J & k & J \\ F' & I & F \end{Bmatrix} {}^{JJ}\rho_{ex\,q}^{\ k} \ . \tag{15}$$

The ${}^{JJ}\rho_{ex}$ matrix is determined by the type of excitation (optical or electronic) which does not act on the spin space. In the present case, where the J moment is aligned parallel to oz, the only nonzero components are $\rho_{ex}{}^0$ and $\rho_{ex\,0}^{\ 2}$. By successively using the expressions (7), (13), (14), and (15) we find an expression for $P(A)$. The ratio $P(A)/P(A=0)$, which is the quantity measured experimentally, allows one to deduce the hfs A:

$$y = \frac{P(A)}{P(A=0)} = \sum_{FF'} \frac{(2F+1)(2F'+1)}{(2I+1)} \times \begin{Bmatrix} J & J & 2 \\ F & F' & I \end{Bmatrix} \frac{(\Gamma^{k=2})^2}{(\Gamma^{k=2})^2 + (E_F - E_F')^2} \ . \tag{16}$$

The amplitude of the repolarization curve is given by

$$(1-y)\,P(H=0, A=0) \ .$$

We present in Fig. 4 the function $y(A)$ for the value $J=I=1$. We can see that the amplitude of the repolarization effect tends to zero when A tends to zero, it increases as A increases and tends to a limit determined by I and J. This formula is equivalent to that of Percival and Seaton[28] but is in a more compact form.

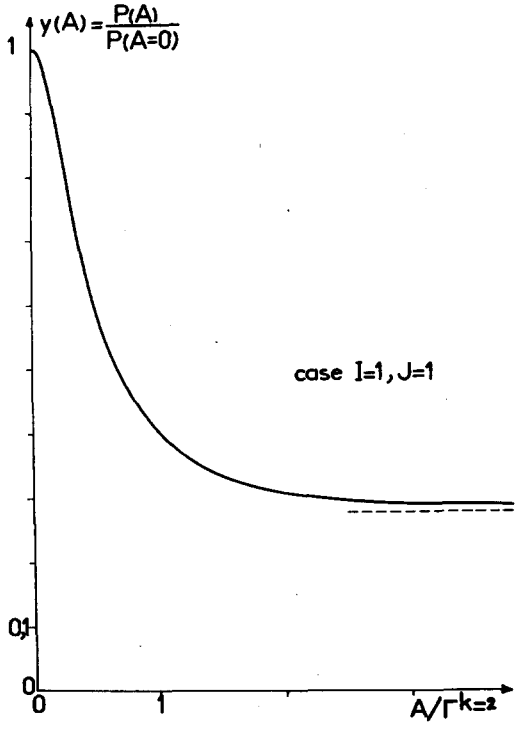

FIG. 4. Evolution of the relative polarization rate $P(A)/P(A=0)$ with the hyperfine structure, in zero magnetic field (case with $I=1$, $J=1$).

3. Experimental determination of A

It follows from the preceding results that, if we can determine experimentally the quantity y for a (I,J) level, we can deduce from the analytical expression of y (16) the value of $A/\Gamma^{k=2}$. This can be done by successively performing a repolarization effect $P(H_z)$ and a Hanle (depolarization) effect $P(H_y)$ (Fig. 2): the amplitude of the repolarization effect is equal to

$$P(H_z=\infty, A) - P(H_z=0, A) \ ,$$

and the amplitude of the Hanle effect is equal to $P(H_y=0, A)$. These two measured quantities give values of

$$P(H_z=\infty, A) = P(H=0,\ A=0), \text{ and } P(H=0, A) \ ,$$

and therefore of y. The $A/\Gamma^{k=2}$ quantity is then determined graphically from $y(A/\Gamma^{k=2})$. We can see from the shape of the curve (Fig. 4) that this graphic determination is not sensitive if $A \ll \Gamma^{k=2}$ or $A \gg \Gamma^{k=2}$.

The hf constant A can then be obtained if the quantity $\Gamma^{k=2}$ of the excited level is known. In the case of weak hfs ($A \ll \Gamma^{k=2}$) the depolarization effect can provide an estimate of Γ if the Lande g_J factor is known: The analytical expression of the Hanle effect established by a calculation in second order in A, similar to that performed in Sec. II, shows that the Hanle width is

$$\Delta H = (\Gamma^{k=2}/g_J\,\mu_B)\,[1 + \text{const.}\ (A/\Gamma^{k=2})^2] \ .$$

If to calculate A from $A/\Gamma^{k=2}$, we take $\Gamma^{k=2} = \Delta H g_J\,\mu_B$, the error is of the order of $(A/\Gamma^{k=2})^2$.

III. EXPERIMENTAL RESULTS

In this section we present the experimental results of the $N=1$, $v=1$ $(1s\,3d)^1\Sigma$ level of H_2, where a weak repolarization effect has been detected; we use the preceding theoretical results to interpret this effect and to obtain the ratio $A/\Gamma^{k=2}$, and A from the repolarization and Hanle effects. The form of the Hamiltonian used in Sec. II ($\mathcal{H}_{hfs} = A\,\mathbf{I}\cdot\mathbf{J}$) is justified in Appendix in the case of the considered $(1s\,3d)^1\Sigma$ level.

A. Experimental conditions

The experimental set up used in this investigation has already been described in a earlier paper.[27,29] The principal characteristics are the following: the hydrogen gas is excited and aligned by an electron beam parallel to oz in a glass triode cell.[30] The grid-plate voltage is 40 V. The emitted light is observed in a direction perpendicular to the beam and analyzed through a monochromator with a resolution of 1.2 Å. The polarization ratio

$$\mathcal{P} = \frac{I(\mathbf{oz}) - I(\mathbf{ox})}{I(\mathbf{oz}) + I(\mathbf{ox})}$$

of the selected line is detected with a double phase sensitive detection system, and is successively measured as a function of static magnetic field H_z (repolarization effect) and H_y (Hanle effect). In the present case, where the polarization ratio is less than 15%, $\frac{2}{3}\mathcal{P}$ can be taken to be the same as the theoretical polarization factor P given by (7), the difference between the experimental and the theoretical ratio y (16) is less than 1% which is within the experimental error. The polarization can be either recorded directly with a x–y recorder or stored with a multichanel analyzer.

B. Results

Several optical transitions of the $(1s\,3d)^1\Sigma \rightarrow (1s\,2p)^1\Sigma$ band have been studied. We report the experimental results for three differents levels: the $N=1$, $v=0$ $(I=1) \rightarrow N=0$, $v=1$ ($\lambda = 4928$ Å); the $N=1$, $v=1$ $(I=1) \rightarrow N=0$, $v=3$ ($\lambda = 5003$ Å); and the $N=2$, $v=1$ $(I=0) \rightarrow N=1$, $v=3$ $\times$ ($\lambda = 5007$ Å).

The polarization ratio was about 15%. Repolarization and Hanle effects have been studied, and give the following results:

(i) $N=1$, $v=0$ $(I=1)$ level: Even with a good signal to noise ratio obtained in the Hanle experiment, no repolarization effect was detected, which places an upper limit of a possible hf structure to be 0. 15 MHz.

(ii) $N=1$, $v=1$ $(I=1)$ level: Figure 5 shows the relative magnitude of the two effects which have been detected. An example of the repolarization curves obtained with the accumulating system is shown in Fig. 6. The small relative amplitude of the repolarization effect corresponds to a case of weak hf structure ($A < \Gamma^{k=2}$) and allows us to use the previous calculations: the experimental curves are fitted to Lorentzian functions. The relative amplitudes thus obtained (respectively equal to $P(A=0) - P(A)$ and to $P(A)$ in the repolarization and Hanle effects) enable us to determine the ratio $y = P(A)/$

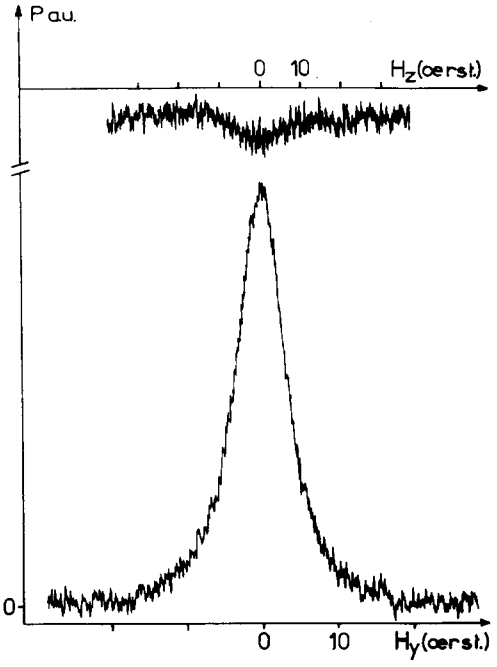

FIG. 5. Repolarization (a) and Hanle (b) effects in the $N=1$, $v=1$ $(1s\,3d)^1\Sigma$ level of H_2, obtained with a x–y recorder using a lock in amplifier time constante of 3 sec.

$P(A=0)$ and hence $A/\Gamma^{k=2}$ from the theoretical curve of y as a function of $A/\Gamma^{k=2}$(Fig. 4). The value of $\Gamma^{k=2}$ is obtained from the Hanle experiment, taking the g value of 0.606 given by Dieke[31] enabling us to calculate the hf constant A. The values obtained are given in Table I after averaging of many experiments performed at the same gas pressure (2.10^{-2} torr). The hf constant thus obtained is $A=1\pm0.17$ MHz, which is about six times smaller than the natural width Γ.

(iii) $N=2$, $v=1$ $(I=0)$ level: As predicted $(I=0)$, no signal was detected in the repolarization experiment.

C. Discussion

1. Results

Different effects can perturb the experimental determination of y (16), and must be discussed in order to qualify the preceding results:

(i) Parasitic Hanle effects can occur, which could create an effect of the same shape as the repolarization effect when on sweeping the magnetic field H_z, even in the absence of any repolarization effect. This can happen for example if the electron beam is not exactly parallel to H_z, or if the earth's magnetic field components H_x or H_y are not properly compensated. This possibility is excluded by the experimental results obtained on the $N=2$ $(I=0)$ level where no variation (H_z) was detected.

(ii) The main uncertainty in this kind of measurements is the possiblility of cascades. The fact that the width of the Hanle and of the repolarization curves have the predicted $\frac{1}{2}$ ratio shows that the two phenomena are created in the same level. Nevertheless, these experiments alone cannot rule out the possibility that both signals come from a same cascading electronic level, which could cascade on all the observed rotational sublevels. This last possibility is ruled out however by another experiment performed in the $N=1$, $v=0$ level[32]: this magnetic resonance experiment shows that the Lande g factor is the same as that measured by optical spectroscopy by Dieke,[31] and that the Hanle width agrees with the zero hf field extrapolated width of the magnetic resonance. This agreement is a strong indication that the Hanle effect (and thus the repolarization effect) is not due to a cascade.

2. Origin of the hfs

The origin of the hfs of the $N=1$, $v=1$ $(1s\,3d)^1\Sigma$ level is not known at present. If the level were a pure $^1\Sigma$ state (corresponding to a pure "b" Hund's coupling[33]) no hfs would occur, and the g factor would be of the order of magnitude of a nuclear g factor (10^{-3}). The weak hfs can therefore have two different origins:

(i) A $^1\Sigma-(^1\Pi, ^1\Delta)$ mixture, corresponding to an intermediate "b–d" Hund's coupling (the nuclear spin–orbit in the $\Lambda\neq0$ state is then responsible for the hfs in the $^1\Sigma$ state).

(ii) A singlet–triplet mixture (the contact interaction in the triplet state is then responsible for the hfs in the singlet state); a similar phenomenon has been observed in atomic He.[34]

To determine the contribution of each process is beyond the scope of this paper; we just wish to point out here the main difficulties arising in such a study.

The first case (i) has been discussed by different authors and is responsible for the g factor values of the order of unity instead of zero. Different calculations based on the mixture of the $(1s\,3d)^1\Sigma$, $^1\Pi$, $^1\Delta$ states have been carried out[35–37] in order to determine the exact intermediate coupling scheme. Despite the different approaches the calculated and measured[31,32,37] g factor values differ by about 20%. This discrepency suggests that some other neglected singlet states may have an important contribution. Therefore we cannot base a precise calculation of hfs on these intermediate coupling calculations.

In the second case (ii), the singlet–triplet energy separation is not known exactly because of a discrepency between the theoretical[38,39] and the experimental[31,33,40] results (the experimental energy levels of the triplet states must be lowered by some 150 cm^{-1} to be in agreement with the theoretical values) no exact calculation of the mixture can therefore be carried out.

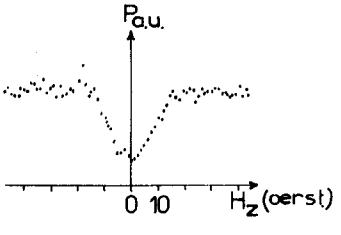

FIG. 6. Repolarization effect in the $N=1$, $v=1$ $(1s\,3d)^1\Sigma$ level of H_2, obtained by an averaging system for 640 sweeps of 100 sec. The arbitrary units used here are not consistent with these one used in Fig. 5.

TABLE I. Experimental results of the $N=1$, $v=1$ $(3d)^1\Sigma$ of H_2. $\tau=(\Gamma^{k=2})^{-1}$ represents the lifetime of the alignment ρ^k in the excited state.

	Amplitude (a.u.)	$\frac{P(A)}{P(A=0)}$	$A/\Gamma^{k=2}$	ΔH (oersted)	$\Gamma^{k=2}$ (sec^{-1})	τ(sec) ($p=2.10^{-2}$ torr)	A(MHz)
Hanle effect	710 ± 10			7.9 ± 0.3	$(4.2\pm0.15)10^7$	$(2.38\pm0.1)10^{-8}$	
		0.917 ± 0.02	0.15 ± 0.02				1 ± 0.17
Repolarization effect	63 ± 1			19.7 ± 1.2			

IV. CONCLUSION

In this paper, we have studied the experiments that can be used to measure a hyperfine structure smaller than the natural width. We have shown that in the case in which we cannot orient the nucleus, as in our molecular studies, the phenomenon which is of lowest order in the hyperfine constant A is the familiar repolarization effect. We present a detailed theoretical study of this effect which enables us to give formulas in closed form for the evaluation of the hfs from the experimental measurement. This method differs from previous ones proposed by other authors in its experimental simplicity.

A preliminary set of experiments has been made on some levels of $(1s\,3d)^1\Sigma$ state of molecular H_2 which give the following results: $A<0.15$ MHz for the $N=1$, $v=0$ level; $A/\Gamma^{k=2}=0.15\pm0.02$ and $A=1\pm0.17$ MHz for the $N=1$, $v=1$ level.

APPENDIX

In this appendix we wish to show that the effective Hamiltonian, for the hyperfine structure of the $3d\,^1\Sigma$ levels we have studied, is of the form $A\,\mathbf{I}\cdot\mathbf{J}$, and does not contain terms in $(\mathbf{I}\cdot\mathbf{J})^2$. It can be seen by inspection of the formulas of Jette and Cahill[41] that for pure singlet and pure Σ (b Hund's case) levels, the hyperfine structure is zero, and then that any observed hfs comes from the breakdown of one of the preceding hypotheses:

If the level is not pure Σ (intermediate b–d Hund's case), as has been indeed shown by various authors[35–37] the admixture of $3d\,^1\Pi$ and $3d\,^1\Delta$ levels brings into the $^1\Sigma$ level part of the hyperfine Hamiltonian of these levels whose only nonzero term is[41]:

$$\mathcal{H}_L=2g_I\mu_0\mu_N\sum_{\alpha,j}(\mathbf{l}_{\alpha j}\cdot\mathbf{I}_\alpha)/r^3_{\alpha j}\ ,$$

which, within a good b Hund's case level, is equal to

$$\mathcal{H}_N=a\Lambda^2\frac{\mathbf{N}\cdot\mathbf{J}}{N(N+1)}\frac{\mathbf{I}\cdot\mathbf{J}}{J(J+1)}=A\,\mathbf{I}\cdot\mathbf{J}\ .$$

If there is singlet–triplet mixing, analogous to that which has been shown to constitute the bulk of the hfs of the corresponding 3^1D level of helium, the analysis is more complicated; we shall use a second order perturbation analysis. Let us call $|(N,S)\,J,I)\,Fm_F\rangle$ the Russel–Saunders basis vectors in which the electronic orbital plus nuclear rotational momentum N is coupled with the electronic spin S to give J, and then J is coupled with the nuclear spin I to give F (scheme of Fig. 1 of Jette and Cahill[41]). Taking into account the fact that fine and hyperfine structure are of the same order of magnitude so that J is not a good quantum number, but neglecting singlet–triplet mixing so that S remain a good quantum number, we obtain the basis vectors for the triplet

$$|((N,1)J,I)\,Fm_F)=\sum_{J'}C^F_{JJ'}\,|((N,1)J',I)\,Fm_F\rangle\ .$$

These have been calculated, for example, in the paper by Jette and Cahill for the $2p\,^3\Pi_u$ level, and we will take them as our zeroth-order basis vectors.

Now, we introduce the part of the spin-orbit plus spin-other-orbit $\mathcal{H}_{so}$ and hyperfine $\mathcal{H}_{hfs}$ Hamiltonians which are not diagonal in S (the spin–spin fine structure Hamiltonian is diagonal in S because it is invariant when one interchanges the orbital positions of the two electrons without interchanging their spins). The second order energy of the singlet level is

$$E^{(2)}(F)=\sum_{J'F'm_{F'}}\{\langle((N,0)J,I)\,Fm_F\,|\mathcal{H}_{so}+\mathcal{H}_{hfs}\,|((N,1)J'I)F'm_{F'})$$
$$\times\langle((N,1)J',I)\,F'm_{F'}\,|\mathcal{H}_{so}+\mathcal{H}_{hfs}\,|((N,0)J,I)\,Fm_F\rangle\}$$
$$\times1/[E(\text{singlet})-E((N1)J',IF')]\ .$$

(In fact, the only nonzero elements have $F=F'$ and $m_F=m_{F'}$ but we keep the full relation for convenience in the discussion.) To first order in the ratio (fine or hyperfine structure)/(singlet–triplet separation) we may use a single energy denominator $E(\text{singlet})-E(\text{triplet})$. We may then use the closure relation

$$\sum_{J'}|((N,1)J',I)\,F'm_{F'})\langle((N,1)J',I)\,F'm_{F'}|$$
$$=\sum_{J'}|((N,1)J',I)\,F'm_{F'}\rangle\langle((N,1)J',I)F'm_{F'}|\ ,$$

and taking into account the fact that $\mathcal{H}_{so}$ does not act upon nuclear variables we obtain that the quadratic $\mathcal{H}_{so}\mathcal{H}_{so}$ term gives no contribution to the hyperfine structure.

Let us now study the cross term $\mathcal{H}_{so}\mathcal{H}_{hfs}$. $\mathcal{H}_{hfs}$ is of the form $\mathbf{O}\cdot\mathbf{I}$ where $\mathbf{O}$ is a vector operator of electronic variables and of the position of the nuclei, i.e., a vector operator in the J space. On the other hand,

$$P\mathcal{H}_{so}=\sum_{J'F'm_{F'}}\frac{|((N,1)J',I)\,F'm_{F'}\rangle\langle((N,1)J',I)\,F'm_{F'}|}{E(\text{singlet})-E(\text{triplet})}\mathcal{H}_{so}$$
$$=\sum_{J'm_{J'}}\frac{|(N,1)J'm_{J'}\rangle\langle(N,1)J'm_{J'}|}{E(\text{singlet}-E(\text{triplet})}\mathcal{H}_{so}\sum_{m_I}|Im_I\rangle\langle Im_I|$$

is unity in nuclear spin space and is a scalar in J space.

$P\mathcal{H}_{so}\mathbf{O}$ is then a vector in J space, and according to the Wigner Eckart theorem is proportional to J within the $|(N,0), Jm_J\rangle$ level, so that the effective Hamiltonian is indeed of the form $A\mathbf{I}\cdot\mathbf{J}$.

The only term left is then the $\mathcal{H}_{hfs}\mathcal{H}_{hfs}$ term which is quadratic in I and then may give a contribution which would not be of the correct form. Since $\mathcal{H}_{so}$ and $\mathcal{H}_{hfs}$ in H_2 are of the same order of magnitude we cannot neglect this term in comparison with the preceding one, but we shall demonstrate that in fact it gives no contribution to the hfs. In $\mathcal{H}_{hfs}$, we shall consider only the main (Fermi-contact) component of the form $C(\mathbf{s}_1\cdot\mathbf{I}+\mathbf{s}_2\cdot\mathbf{I})$ where C is an operator in N space, and $\mathbf{s}_1$ and $\mathbf{s}_2$ the two electronic spins. Taking into account the fact that $\mathbf{s}_1\cdot\mathbf{I}$ has no matrix element within the singlet state, we can write the relevant contribution of $E^{(2)}(F)$ as

$$E^{(2)}(F)=\frac{C^2}{E(\text{singlet})-E(\text{triplet})}\langle((N,(\tfrac{1}{2},\tfrac{1}{2})0)J,I)Fm_F|\mathbf{s}_1\cdot\mathbf{I}$$
$$\times\sum_{J'S'F'm_{F'}}|((N,(\tfrac{1}{2},\tfrac{1}{2})S')J',I)F'm_{F'}\rangle$$
$$\times\langle((N,(\tfrac{1}{2},\tfrac{1}{2})S')J',I)F'm_{F'}|$$
$$\times\mathbf{s}_1\cdot\mathbf{I}|((N,(\tfrac{1}{2},\tfrac{1}{2})0)J,I)Fm_F\rangle$$
$$+(\text{analogous terms for }\mathbf{s}_2\text{ and cross terms between }\mathbf{s}_1\text{ and }\mathbf{s}_2).$$

The central term is a Dirac one over the space N, s_1, s_2, I and can be discarded, so that we can write

$$E^{(2)}(F)=C^2/[E(\text{singlet})-E(\text{triplet})]$$
$$\times\langle((N,(\tfrac{1}{2},\tfrac{1}{2})0)J,I)Fm_F|(\mathbf{s}_1\cdot\mathbf{I})(\mathbf{s}_1\cdot\mathbf{I})$$
$$\times|((N,(\tfrac{1}{2},\tfrac{1}{2})0)J,I)Fm_F\rangle\ ,$$

we then use the relation

$$(\mathbf{s}_1\cdot\mathbf{I})(\mathbf{s}_1\cdot\mathbf{I})=\sum_{K=0}^{2}\sum_{Q=-K}^{+K}(-)^{Q+2-K}[\mathbf{s}_1\times\mathbf{s}_1]^{[K]}_{Q}[\mathbf{I}\times\mathbf{I}]^{[K]}_{-Q}\ ,$$

with the definition of tensorial operator[42]

$$[\mathbf{s}_1\times\mathbf{s}_1]^{[K]}_{Q}=\sum_{qq'}\langle 1q\,1q'|KQ\rangle s_{1q}s_{1q'}\ ,$$

which can be proved using the definition and the closure properties of Clebsh–Gordan coefficients.

Now the spin space tensorial operator

$$[\mathbf{s}_1\times\mathbf{s}_1]^{[K]}_{Q}$$

cannot have nonvanishing matrix element within a singlet ($S=0$) spin space if K and Q are not equal to zero. Consequently, within the singlet space

$$(\mathbf{s}_1\cdot\mathbf{I})(\mathbf{s}_1\circ\mathbf{I})=\tfrac{1}{3}(\mathbf{s}_1)^2(\mathbf{I})^2\ ,$$

so that this term gives no contribution to hyperfine structure.

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